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# Electrochemical oxidation of pesticide polluted drainage water in its natural matrix

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## Abstract

Polluted drainage water from a dump of toxic chemical waste containing organophosphoric pesticides and their natural degradation products was treated with electrochemical oxidation in order to investigate the applicability of the technique in remediation of natural complex polluted water. The dump is located adjacent to the sea in sand dunes, the natural salinity of the investigated water was 0.7<sup>w/w</sup>% and sodium chloride served as main electrolyte. A commercial available flow cell with a tubular design, Ti/Pt<sub>90</sub>-Ir<sub>10</sub> anode, and 316 SS cathode was applied, and the electrolysis experiments were conducted in a batch recirculation experimental set-up. COD measurements showed that the overall oxidation of organic and inorganic substances followed first order kinetics by the current densities investigated, 310-1131 mA cm<sup>-2</sup>, and the COD removal rate increased by increased current density and to a minor extent by increased salinity up to 2.0<sup>w/w</sup>%. The target organic pollutants parathion, methyl-parathion, malathion, ethylaminoparathion, paraoxon, and several phosphoric triesters were all degraded during the treatment except O,O,O-triethylphosphoric acid, a compound formed during the electrochemical process with a highly stable low energy structure, rendering it recalcitrant to participate in the oxidation reaction. The degradation of the subjected organics was found to be caused by indirect oxidation by the hypochlorous/hypochlorite pair as the main oxidizing agent, produced by the anodic oxidation of chloride. The study has showed that electrochemical chloride mediated indirect oxidation is a relevant, neat and possible solution for the remediation of organophosphoric pesticide polluted natural water.

*Key Words : Electrochemical oxidation; Pesticides; Methyl-parathion; Parathion; Indirect oxidation*

## 1 Introduction

Organophosphate esters such as methyl-parathion and parathion have been used as alternatives to dichloro-diphenyl-trichloroethane (DDT) and other chlorinated hydrocarbon pesticides. However, the organophosphate esters are not rapidly degraded in natural waters. At 20 °C and pH 7.4, parathion has a hydrolytic half-life of 108 days, and its toxic metabolite, paraoxon, has a similar half-life of 144 days [1]. Various innovative technologies have been proposed for elimination of organophosphoric pesticides. Especially, degradation of methyl-parathion has been examined by photocatalysis [2,3], hydrogen peroxide [4], ultrasonic radiation [1] or hydrolysis promoted by mercury [5]. The major disadvantage of these technologies is that they are designed for decontamination of aqueous solutions with a very low pollutant concentration and are not suitable for treatment of higher concentrations of pesticides.

Treatment of recalcitrant toxic waste waters by electrochemical methods has gained more and more interest in the recent years [6-14]. In the electrochemical treatment, the organic and toxic pollutants are oxidized by direct electron transfer at the surface of the anode and by indirect oxidation via production of oxidants such as hydroxyl radicals and hypochlorite, corresponding to the models proposed by Comninellis [6;7] and De Battisti [8]. Electrochemical treatment has been successfully applied in the purification of domestic sewage [9], landfill leachate [10,11], tannery wastes [12], olive oil waste waters [13], textile dyes [14] etc. For a comprehensive review of electrochemical processes in waste water treatment please refer to [15].

Electrochemical oxidation of organophosphoric pesticides has in prior studies been investigated with methyl-parathion as the model pollutant. In pure solution with sodium chloride as electrolyte, 80 % reduction of both COD and BOD was obtained with a mean energy consumption of 8-18 kWh (kg COD<sub>r</sub>)<sup>-1</sup> [16]. Furthermore, the investigation showed that methyl-parathion degradation was far

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more effective, when the brine solution was in the acidic range. The investigation was conducted in a laboratory scale plant using Ti/Pt as anode and SS 304 as cathode. Through a factorial experimental procedure, the electrolysis efficiency was optimized and upgraded to electro-Fenton through addition of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and the final process resulted in a satisfactory removal of organic load with a significant improvement of the COD/BOD<sub>5</sub> ratio, rendering the effluent amenable to biological treatment [17]. An investigation of the degradation pathways of methyl-parathion in aqueous solution by electrochemical oxidation has showed a rapid degradation, but without full mineralization of all methyl-parathion [18]. Several intermediates were identified with oxalic, formic and acetic acids as well as tetraphosphorus trisulfide as final products [18]. However, it has not yet been clarified whether direct or chlorine mediated oxidation is the most important mechanism in the degradation of methyl-parathion. So far, both mechanisms seem to play an important role, but the fact that additional sodium chloride in the present work increased the degradation and incomplete mineralization of methyl-parathion was obtained in previous studies [18] might indicate the importance of the indirect oxidation, due to a higher selectivity of hypochlorite oxidation.

In this study, the electrochemical treatment of a complex mixture of organophosphoric pesticides and naturally occurring degradation products from the pesticides in aqueous solution was investigated. The investigated matrix was polluted drainage water, directly sampled from a dump of toxic chemical waste originating from a large scale industrial production of pesticides. The dump was located in sand dunes adjacent to the sea. In comparison with the prior investigations of methyl-parathion degradation [16-18] in model solutions, the concentrations of the individual substances were low and the complexity of the matrix was high with regards to the presence of naturally occurring salts and impurities. However, the successful conclusions from the prior research [16-18] render electrochemical oxidation as being a promising technique in remediation of the subjected water pollution. The aim of the study was to investigate the applicability of the electrochemical oxidation technique for remediation of natural water polluted with organophosphoric pesticides, the influence of salinity and current density on the rate of COD removal, current efficiency, and energy consumption, and to determine the importance of the indirect oxidation by hypochlorite. The latter aspect is important regarding the practical applicability of the electrochemical oxidation, since treatment of a higher capacity of water at lower cost is possible if intermixing of the drainage water and electrochemically generated oxidant is workable. Hence, the present study was conducted as a part of providing a basis for decision concerning the future remediation strategy of the polluted site.

## **2 Materials and methods**

### **2.1 Applied materials and the electrochemical cell**

The dump was located adjacent to the sea and hence a high salinity of 0.7 % w/w was initially present in the investigated drainage water. The natural conductivity is 9.51 mS cm<sup>-1</sup> rendering the water amenable to electrochemical treatment. The natural pH of the drainage water was 4.2 with a high concentration of dissolved iron of 59.8 mg L<sup>-1</sup>. The sodium chloride used to increase the salinity was of technical grade approved for use in foodstuff. The applied electrochemical flow cell was a laboratory scale commercially available cell from Watersafe. The cell has a tubular design with bottom inlet and top outlet. The applied rod-like anode was made of solid titanium coated with a 90-10% alloy of platinum and iridium, respectively, and the cathode was 316 stainless steel. The cell had a specific volume of 43 ml with an anode surface of 60.3 cm<sup>2</sup> and an electrode gap of 3 mm.

### **2.2 Experimental procedure**

The electrochemical treatment of the drainage water was investigated in a water cooled batch recirculation system. The water was pumped through the cell at a flow rate of 430 L h<sup>-1</sup> from a

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stirred tank with a volume of 25 L. The overall cell voltage was controlled by an external power supply. Prior to start of each experiment, the 25 L batch of drainage water was recirculated without applied voltage for 10 min. in order to ensure homogenization and that no autocatalytic activity was found by the anode surface. During the experimental run, water was sampled from the tank for further analytical determination. The experiments were conducted at a constant temperature of 13 °C if nothing else is specified. The investigated current densities range from 310-1131 mA cm<sup>-2</sup>, the overall cell voltage from 8.0-20.0 V and the salinity from the natural level of 0.7 w/w % up to 4.0 w/w %.

### 2.3 Analytical methods

Parameters as oxidation and reduction potential (ORP), pH, temperature, conductivity and dissolved oxygen (DO) were monitored in the bulk solution in the tank by appropriate sensors. Analysis of the chemical oxygen demand (COD) of the sampled water was conducted by the Merck Spectroquant spectrophotometric method approved by USEPA. Analytical determination of the concentration of dissolved iron was performed by atomic absorption spectroscopy (AAS, Perkin Elmer MHS-10). Determination of the concentration of the parent pesticides parathion, methyl-parathion, malathion and a range of degradation products were performed by Gas Chromatography with an NPD detector.

## 3 Results and discussion

The electrochemical oxidation of the pesticide polluted drainage water has been performed galvanostatically under different experimental conditions of salinity and current density. Due to the kinetic evaluation of the COD removal rate, the results are presented versus the time scale and not specific charge passed. However, the axes are easily transformed due to the fixed investigated water volume of 25 L. By a current density of 310 mA cm<sup>-2</sup>, 180 min corresponds to 2.24 Ah L<sup>-1</sup>.

In figure 1a and 1b, the dependencies of the COD removal rate on salinity and current density are showed. COD was under all experimental conditions removed to the detection limit within 100 min, however some differences were observed. Through standard kinetic modeling to zero, first, and second order expressions, it was found that the overall COD removal rate in the majority of experiments could be fitted to first order dependencies of the COD concentration with squared correlation coefficients,  $R^2$ , from 0.9810-0.9993.

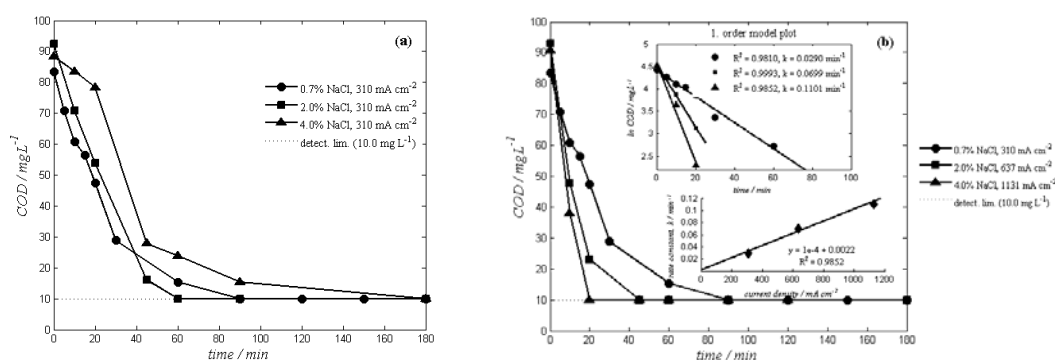


Figure 1: (a) Evolution in COD during electrolysis by increased salinities at constant current density of 310 mA cm<sup>-2</sup>. (b) Evolution in COD during electrolysis by increased salinities and current densities.

An increase in salinity at a constant current density of 310 mA cm<sup>-2</sup> enhanced the COD removal rate up to 2.0 w/w % probably due to an increased production of hypochlorous acid, the predominant chlorine species in the pH range investigated (fig. 1a). However, a further increase in salinity to 4.0 w/w % showed a reverse effect on the COD removal rate, which significantly deviated from the first order reaction model. The unexplained kinetics observed at the higher sodium chloride concentration might be explained by the established competition between the lower overpotential chloride oxidation and the discharge of water generating MO<sub>x+1</sub> at the anode surface. The chloride

oxidation may become the main process, and as the bulk oxidation rate of COD by chlorine is slower than the surface oxidation rate by  $\text{MO}_{x+1}$ , the COD removal shows a sluggish decay. In addition, the high concentration of negatively charged chloride ions may inhibit the transport of the chloride oxidation product away from the anode, an effect enhanced by the condensation of the diffusive part of the double layer, as a result of the increased electrolyte concentration and ion strength of the solution. In the latter case, the formed hypochlorous acid/hypochlorite might be further oxidized to chlorate and other chlorine species with only minor oxidizing capability towards COD at the present conditions. During the experiment conducted at 4.0 w/w% salinity, the overall cell voltage was reduced to 8.0 V in order to maintain constant current density, but the electrode potential was still considered well above the needed anode potential for chloride electrolysis, taken account of overpotential effects. In total, the COD removal only showed a minor dependence on the salinity at constant current density indicating that the current density acted as limiting step in the removal of COD (fig. 1a). This indication was supported when the overall applied cell voltage was kept constant at the 19 V level at the higher salinities with only minor voltage regulations to maintain constants current densities during the experiments (fig. 1b). Due to the highly increased conductivity of the solution, the current densities increased significantly and a corresponding increase in COD removal rate was observed. In addition, the increased current density drove the electrooxidation process to a mass transfer controlled situation following first order kinetics even at 4.0 w/w% salinity. A more or less linear correlation between current density and the COD removal rate constant was found, probably due to a zero order relationship between hypochlorous acid/hypochlorite formation and current density in the electrolysis process found in prior studies (not published). This observation again indicated the importance of the indirect oxidation of the present COD by hypochlorous acid/hypochlorite. When COD was plotted with respect to the amount of specific charge ( $\text{Ah L}^{-1}$ ) added to the solution during the electrolysis, the COD evolution was unaffected by the increasing current densities (plot not showed). Hence the level of COD removal only depended on the amount of charge added, an observation in agreement with prior studies of chloride mediated indirect oxidation of 2-naphtol [20].

The results of the analysis of the concentration of the specific organophosphoric pesticides and degradation product during the electrochemical treatment at  $310 \text{ mA cm}^{-2}$  and 0.7 w/w% are seen in figure 2a, b, and c. The parent pesticides methyl-parathion, parathion, and malathion were readily degraded within 30 min (fig. 2a) whereas paraoxon, a toxic degradation product of parathion not present in measurable amounts in the natural drainage water was formed during the oxidation of parathion (fig. 2b). It was eliminated after 180 min. The decrease in concentration was observed once the parent compound parathion was removed from solution. Other degradation products as ethylaminoparathion and O,O,S-trimethyl-dithiophosphoric acid initially present in highest concentrations ( $3.1\text{--}3.5 \text{ mg L}^{-1}$ ) of the organics monitored in the drainage water were readily degraded as well (fig. 2b).

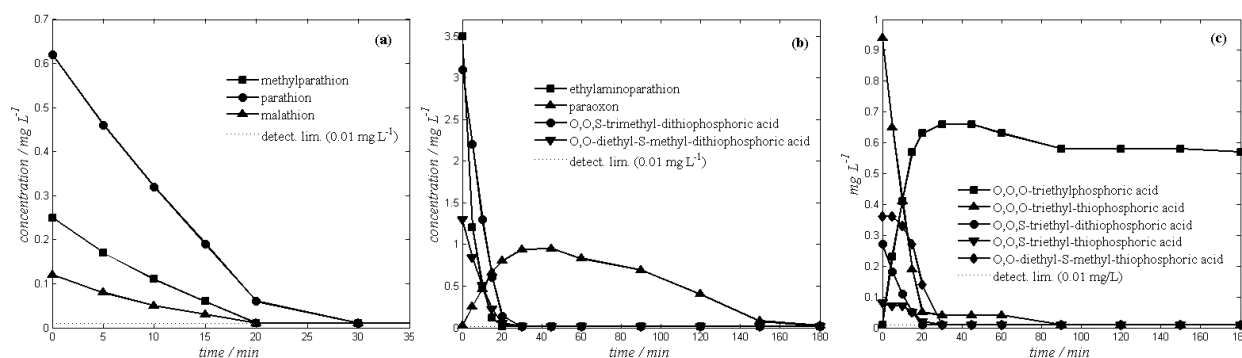


Figure 2: (a) Degradation of the parent pesticides during electrolysis at 0.7 w/w% salinity and  $319 \text{ mA cm}^{-2}$  current density. (b) and (c) Evolution in the degradation products.

A single triester showed a more recalcitrant behavior. O,O,O-triethylphosphoric acid was formed during the electrolysis as the double bonded sulfur atom on O,O,O-triethyl-thiophosphoric acid was

substituted with oxygen, a process which apparently formed a more stable triester that were not significantly affected by either the hypochlorous acid/hypochlorite oxidation or direct oxidation at the anode surface (fig. 2c). 79% of O,O,O-triethyl-thiophosphoric acid was oxidized to O,O,O-triethylphosphoric acid, the last part is expected to be converted to O,O-diethyl-thiophosphoric acid and ethanol by hydrolysis. O,O,S-triethyl-thiophosphoric acid, a compound with similar side chains and structure, but with sulfur forming one of the ester bonds, was oxidized during the process without obstacles. The influence of the presence of the sulfur atom in the considered triester compounds on the stability and the reactivity towards oxidation reactions was investigated by quantum mechanical computational calculations of the internal energies of the molecules in vacuum. It was found that the length of all phosphorous oxygen bonds in the triester was shortened due to the change from a polarisable sulphur atom to a double bonded and hard oxygen atom which also has a shorter bond length to the phosphorous atom. The result of this change is a more stable molecule and probably therefore also a more recalcitrant molecule to the oxidation process.

The fact that the organophosphoric pesticides are oxidized due to the chloride mediated indirect electrochemical oxidation process is of significant practical use, since the required oxidant solution can be generated on site from the adjacent sea water and transportation of chemicals can be limited. The results obtained in the study also suggest possibilities for applying the electrochemical generated oxidant solution for remediation of the polluted soil by injection into the formation. However, this application requires more intensive pilot scale studies to be performed prior to practical use.

## 4 Conclusions

In this paper, the electrochemical treatment of drainage water sampled from a dump of toxic chemical waste and polluted with organophosphoric pesticides and several naturally occurring degradation products was investigated under different experimental conditions. Electrolysis performed in a batch recirculation setup has showed that the present COD was efficiently depleted within time scales of practical use and the removal rate increased with increased current density and to a minor extent by increased salinity up to 2.0 ‰. The subjected pesticides parathion, methyl-parathion, malathion and degradation products ethylaminoparathion, paraoxon and several triesters were all degraded during the electrolysis except O,O,O-triethylphosphoric acid due to a highly stable low energy structure surrounding the central phosphorous atom, rendering it recalcitrant towards oxidation. The degradation of the subjected organics was found to be caused by chloride mediated indirect oxidation by the hypochlorous/hypochlorite pair as the main oxidizing agent. The study has showed that electrochemical chloride mediated indirect oxidation is a relevant, neat and possible solution for the remediation of organophosphoric pesticide polluted natural water.

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